

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
18 March 2004 (18.03.2004)

PCT

(10) International Publication Number  
**WO 2004/022229 A1**

(51) International Patent Classification<sup>7</sup>: **B01J 29/08**,  
29/14, 29/16, 29/40, 29/46, 29/48, 29/65, 29/68, 29/69,  
29/70, 29/76, 29/78

(74) Agent: LEVY, Harry M.; Emrich and Dithmar, 300 South  
Wacker Frive, 3000, Chicago, IL 60606 (US).

(21) International Application Number:  
PCT/US2003/007047

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE,  
SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN,  
YU, ZA, ZM, ZW.

(22) International Filing Date: 7 March 2003 (07.03.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
PCT/US02/28019  
4 September 2002 (04.09.2002) US

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,  
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,  
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant: **THE UNIVERSITY OF CHICAGO**  
[US/US]; 5801 South Ellis Street, Chicago, IL 60635  
(US).

**Published:**  
— with international search report

(72) Inventors: **MARSHALL, Christopher, L.**; 1508 Lark  
Ln., Naperville, IL 60565-1305 (US). **NEYLON, Micheal,**  
**K.**; 724 Benedetti Drive, Naperville, IL 60563-8979 (US).

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: NOVEL CATALYST FOR SELECTIVE NO<sub>x</sub> REDUCTION USING HYDROCARBONS

(57) Abstract: A two phase catalyst is disclosed with one or more transition metals such as Cu, Co, Fe, Ag and Mo supported on a molecular sieve having a pore size not greater than 8 Å along with a stabilized oxide of one or more of the oxides of Zr, Mo, V, Nb or the rare earths coating the molecular sieve. A method of preparing the two phase catalyst and using same to remediate NO<sub>x</sub> in combustion gases is also described.

WO 2004/022229 A1

BEST AVAILABLE COPY

**NOVEL CATALYST FOR SELECTIVE NO<sub>x</sub>  
REDUCTION USING HYDROCARBONS  
CONTRACTUAL ORIGIN OF THE INVENTION**

The United States Government has rights in this invention pursuant to Contract No. W-31-109-ENG-38 between the U.S. Department of Energy (DOE) and The University of Chicago representing Argonne National Laboratory.

**RELATED APPLICATIONS**

This application is a continuation-in-part of U.S. patent application serial no.09/975,708 filed October 11, 2001.

**FIELD OF THE INVENTION**

The present invention relates to the reduction of nitrogen oxides (NO<sub>x</sub>) present in a lean burn exhaust by the selective catalyst reduction of NO<sub>x</sub> by a hydrocarbon with a bifunctional catalyst.

**BACKGROUND OF THE INVENTION**

The combustion of fossil fuels unavoidably leads to the formation of nitrogen oxides (NO<sub>x</sub>) which, if released to the atmosphere, can lead to acid rain and detrimental interactions with ozone. Increasing government regulations around the world have called for continued NO<sub>x</sub> emission reductions from both stationary and mobile sources, requiring new and improved technologies that can remove NO<sub>x</sub> from exhaust streams. While three-way catalysts have been optimized to reduce NO<sub>x</sub> emissions in rich-burn exhaust as from consumer automobiles, these catalysts are ineffective under lean-burn conditions, as usually observed with stationary sources or diesel engines. Reduction of NO<sub>x</sub> with ammonia has been used industrially for stationary sources. However, it is less desirable (especially in transportation systems) due to the toxic nature of the ammonia which must be stored locally. Alternative catalytic processes have been investigated for operation under lean burn conditions, with the selective catalytic reduction (SCR) of NO<sub>x</sub> with hydrocarbons being one of the most promising. These hydrocarbons are more readily available and pose less of an emission problem.

A large number of materials have been found to be catalytically active for SCR. By far, the most widely reported in the open literature are metal-exchanged zeolites,

such as Cu-ZSM-5, Co-ZSM-5, and Fe-ZSM-5. These have been found to be very active for SCR using C<sub>3</sub> hydrocarbons, with Cu-ZSM-5 being the most active. However, the zeolite-based materials lose much of their activity when water (common in exhaust streams) is added to the exhaust stream. The exact effects of water are not well known; it is speculated that either dealumination of the zeolite framework occurs which reduces the number of active sites, or that the metal sites agglomerate or are over-oxidized and lose their activity. While other catalysts that possess greater water stability have been found, such as metal-supported oxides, these tend to lack the desired activity seen by the metal zeolites, and produce large amounts of N<sub>2</sub>O (also a major pollutant).

Patents which have varying relationships to the inventions at issue are, for instance, U.S. patent no. 5,116,586 issued to Baacke et al., May 26, 1992. This patent relates to a zeolite catalyst and a method for reduction of nitrogen oxides by mixing the waste gas with ammonia. As previously discussed in the background of this invention, the use of ammonia in the reduction of nitrogen oxide requires entirely different conditions than the present invention which is an NO<sub>x</sub> reduction catalyst utilizing hydrocarbons. The Baacke et al. patent does not show or suggest a two phase catalyst or the method of making the inventive two phase catalyst, nor obviously, the present catalysts themselves in which the stabilizing oxide coats the molecular sieve or zeolite material. Moreover, the use of ammonia itself presents a hazard.

The Green et al. U.S. patent no. 4,962,075 issued October 9, 1990 discloses a single phase catalyst obtained by intimately mixing the powders of the oxide binder and the metal salts so that although a physical mixture is formed, the inventive two phase catalyst is not made. This patent teaches mixing particles of a metal exchanged zeolite with an oxide. In this case, both particles are usually quite large (500 nm to 50,000 nm) and although the particles physically contact each other, no two phase catalyst with intimate contact between the phases such as produced by the methods of Examples 1-3 hereafter.

The Green et al. U.S. patent no. 5,276,249 issued January 4, 1994 relates to a catalyst composition for the destruction of halogenated organics. The Green et al.

'249 patent like the Green et al. '075 patent does not show or suggest the inventive method of making the two phase catalyst of the present invention, and therefore, does not show or suggest the present inventive catalyst. Although the '075 patent does disclose the use of cerium oxide, the Green et al. '249 patent does not, neither patent teaches the present invention which uses metal oxide sols for creating the second phase.

Also cited in the parent case is the Sachtler et al. U.S. patent no. 6,143,681 issued November 7, 2000. The Sachtler et al. patent uses an entirely different means of introducing the metal into the zeolite, such as by metal vapor deposition, which leaves the metal in a different state and the addition of cerium into the matrix is by ion exchange not by a sol as taught in the present invention. Moreover, the '681 patent does not show or suggest the addition of a rare earth oxide by the use of a sol as opposed to a salt. Therefore, the '681 patent as the other patents cited in the prior case do not show the method of the present invention and therefore do not show the two phase catalyst of the present invention.

#### **SUMMARY OF THE INVENTION**

The present invention is the development of bifunctional catalysts that combine active metal-exchanged molecular sieves along with a separate metal oxide stabilizing phase from a sol precursor forming an oxide coating thereon that offers hydrothermal stability with sustained activity at low temperature for lean burn or rich burn exhaust with or without water present under SCR conditions.

Accordingly, it is a principal object of this invention to provide an effective method and catalyst for the reaction of  $\text{NO}_x$  in lean burn or rich burn exhaust with or without water present.

Yet another object of the invention is to provide a two phase catalyst comprising one or more transition metals supported on a molecular sieve and one or more stabilizing oxides coating the molecular sieve material.

A further object of the present invention is to provide a two phase catalyst comprising contacting a molecular sieve material having a pore size less than about 8 Å with a sol of oxide particles having average diameters of greater than 8 Å and less than about 100 nanometers to coat the molecular sieve particles with the oxide

particles and loading the molecular sieve before and/or after the oxide coating with one or more transition metals.

Another object of the invention is to provide a two phase catalyst comprising a zeolite supported transition metal and a stabilizing oxide coated on the zeolite.

Still another object of this invention is to provide a method of remediating the concentration of nitrogen oxides ( $\text{NO}_x$ ) in the exhaust from lean burn or rich burn combustion in the presence of water in which the exhaust containing water and  $\text{NO}_x$  is contacted with one or more of an organic reductant or mixtures thereof at a temperature of not greater than about  $600^\circ\text{C}$  with a two-part catalyst including a molecular sieve supported transition metal and a stabilizing metal oxide.

A final object of the present invention is to provide a method of remediating the concentration of nitrogen oxides ( $\text{NO}_x$ ) in a combustion exhaust stream by contacting the exhaust stream with one or more organic reductants in the presence of water at a temperature not greater than  $600^\circ\text{C}$  over a two phase catalyst comprising one or more transition metals of Cu, Co, Fe, Ag and Mo supported on a molecular sieve having a pore size not less than  $8 \text{ \AA}$ , preferably between  $4 \text{ \AA}$  and  $8 \text{ \AA}$  and a stabilizing oxide of one or more of the oxides of Zr, Mo, V, Nb or the rare earths.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a graphical representation of the conversion of  $\text{NO}_x$  and propene as a function of temperature for a Cu-ZSM-5 catalyst and a  $\text{CeO}_2$ /Cu-ZSM-5 catalyst.

Closed symbols represent conversions under dry conditions, while open symbols represent conversions under wet (10% water) conditions;

FIG. 2 is a graphical representation of the conversion of  $\text{NO}_x$  and propene over a zeolite supported copper catalysts stabilized with ceria illustrating various silicon to aluminum ratios;

FIG. 3 is a graphical representation of the conversion of  $\text{NO}_x$  and propene as a function of temperature for copper supported zeolite stabilized with  $\text{ZrO}_2$  and a copper supported zeolite stabilized with molybdenum oxide;

FIG. 4 is a graphical representation of the conversion of  $\text{NO}_x$  and propene as a function of temperature for a cobalt supported zeolite and a cobalt supported zeolite stabilized with  $\text{CeO}_2$ ;

FIG. 5 is a graphical representation of the conversion of  $\text{NO}_x$  and propene as a

function of temperature for copper supported zeolite stabilized with  $\text{CeO}_2$  and  $\text{ZrO}_2$  and a copper and cobalt supported zeolite;

FIG. 6 is a graphical representation of the conversion of  $\text{NO}_x$  and propene as a function of temperature for a copper supported mordenite and a copper supported mordenite stabilized with  $\text{CeO}_2$ ;

FIG. 7 is a graphical representation of the conversion of  $\text{NO}_x$  and propene as a function of temperature for a physical mixture of Cu-ZSM-5 and  $\text{CeO}_2$  and Cu-ZSM-5/ $\text{CeO}_2$ ;

FIG. 8 is a Scanning Electron Micrograph (SEM) Cu-ZSM-5 without the stabilizing oxide; and

FIG. 9 is a SEM of Cu-ZSM-5 with a coating of the stabilizing oxide ( $\text{CeO}_2$ ).

#### **DESCRIPTION OF THE PREFERRED EMBODIMENT**

While the preferred embodiment is generally illustrated by reference to examples involving a catalyst composed of a zeolite supported copper metal impregnated with a ceria stabilizing oxide, it should be understood that a variety of molecular sieve materials are satisfactory including zeolites. Specifically, zeolite Y, zeolite beta, mordenite, ferrierite, ZSM-5, and ZSM-12 are preferred. The molecular

sieve preferably should have a pore size of at least about 4 Å. Moreover, any transition metal would be adequate to be supported by a molecular sieve in a wide variety of concentrations. However, commonly used transition metals are copper, cobalt, iron, silver, molybdenum, vanadium and various combinations thereof. Also, the supporting oxides can be any one or more of the rare earth oxides such as cerium oxide and transition metal oxides, such as zirconium oxide, molybdenum oxide, vanadium oxide and niobium oxide. Cerium oxide alone or in combination with one or more of the other rare earth oxides is preferred. All of the preferred oxides are added in the form of metal oxide sols.

Specifically, a wide variety of pore size zeolites has been investigated and it is preferred that the pore size be in the range of from about 4 Å and up to about 8 Å. In the art, these are referred to as medium pore and wide pore zeolites. Investigations have been conducted using various water concentrations up to about 20% by volume. It is believed that the stabilizing oxide may be present in the catalyst in the range of from about 0.1% by weight to in excess of about 40% by weight including the molecular sieve, with about 5% by weight being the minimum preferred and about 20% by weight being most preferred. It is also believed that the typical exchange levels for the transition metal may be anywhere from about 25-200% with 100% being preferred. Moreover, a variety of ratios of silicon to aluminum have been tested in zeolites and found to be satisfactory. Silicon to aluminum ratios found to be satisfactory are generally between about 238 and about 17 to one. While the reductions herein use organics such as propylene ( $C_3H_6$ ) or hexane, any alkane or alkene between  $C_1$  and  $C_{16}$  is acceptable but  $C_1$  to  $C_8$  are preferred. In addition, non-organic reductants such as ammonia or urea are applicable as are organics such as alcohols.

Most of the examples investigated have been using the Cu-ZSM-5 and  $CeO_2$  system. Besides physically mixing these catalysts, the bifunctional catalysts were synthesized in two distinct ways to vary the way the phases were mixed. The methods used here can be easily extended to incorporate a number of oxides, such as the rare earth oxides, zirconium oxide, vanadium oxide, the molybdenum oxides, the niobium oxides or combinations thereof, onto any transition metal-exchanged

zeolite, including but not limited to Co-ZSM-5, Fe-ZSM-5, or Cu-ZSM-5, Ag-ZSM-5, Mo-ZSM-5 as well as the multimetallic-exchanged zeolites. Furthermore, it is believed that other zeolites besides ZSM-5, such as zeolite Y, Beta zeolite, the others synthetic or natural zeolites, or other molecular-sieve-like materials, such as silica-aluminophosphate (SAPO) or MCM-41, could be used as the primary component of the metal support.

#### EXAMPLE 1

*Preparation of CeO<sub>2</sub>/Cu-ZSM-5:* Copper was ion exchanged with a ZSM-5 zeolite via typical means. A 0.01 M solution of Cu(NO<sub>3</sub>)<sub>2</sub> was prepared, and 2 g of H-ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 80) was stirred into 40 ml of the solution. The slurry was stirred overnight at room temperature, then filtered, washed with distilled water, dried at 100°C in a vacuum oven, then calcined in air at 500°C for 3 hrs. Copper loadings can be adjusted by changing the concentration of the solution, the pH of mixing, or by repeated exchanges with the solution. Ceria was introduced by first diluting a ceria sol from 20 wt% to 0.01M. Two grams of the Cu-ZSM-5 was mixed with 40ml of the ceria solution, and was stirred overnight at room temperature. The slurry was filtered, washed, dried, and then calcined using the same conditions above. This catalyst will be referred to as "CeO<sub>2</sub>/Cu-ZSM-5".

#### EXAMPLE 2

*Preparation of Cu-ZSM-5/CeO<sub>2</sub>:* High surface area ceria was first prepared following traditional procedures. Five grams of cerium carbonate was slowly mixed with 4.5 ml of glacial acetic acid to produce cerium acetate. The sample was dried in a vacuum over at 100°C, then calcined in air at 425°C to produce cerium oxide. The ceria was coated with a layer of Al<sub>2</sub>O<sub>3</sub> to act as a template by mixing 2 g of the ceria with 40 ml of a 0.01M Al<sub>2</sub>O<sub>3</sub> sol (diluted from a 20wt% sol), stirring overnight, then filtering, washing, drying, and calcining in air at 500°C as above. The zeolite precursor solution was prepared by mixing a solution containing NaOH, dissolved Al foil, and H<sub>2</sub>O with tetraethylorthosilicate (TEOS) and tetrapropylammonium hydroxide (TPAOH) such that the molar concentrations in the final solution was 4:0.06:571:6:1 NaOH:Al:H<sub>2</sub>O:TEOS:TPAOH. The solution was stirred at room temperature overnight, then approximately 40 ml was added to 2 g of the Al<sub>2</sub>O<sub>3</sub> coated ceria in an



autoclave. The autoclave was heated to 175°C for 6 hrs under autogenic pressure. After rapid cooling, the sample was filtered, washed, dried, then calcined for 6 hrs in air at 500°C to remove residual organic compounds. Copper was exchanged with the zeolite film/ceria following the methods listed above for CeO<sub>2</sub>/Cu-ZSM-5. The final catalyst will be referred to as "Cu-ZSM-5/CeO<sub>2</sub>".

### EXAMPLE 3

In addition to the catalysts above, additional catalysts tested included: a Cu-ZSM-5 prepared similarly to CeO<sub>2</sub>/Cu-ZSM-5 but without ceria addition, and a quantity of the Cu-ZSM-5 catalyst mixed in a equal weight ratio with the high surface area ceria prepared above. This latter catalyst was mixed by gentle grinding in a mortar for about 10 minutes.

### EXAMPLE 4

*Preparation of Cu-ZSM-5 and CeO<sub>2</sub>/Cu-ZSM-5 of various SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios:* These materials were prepared similarly to the Cu-ZSM-5 and CeO<sub>2</sub>/Cu-ZSM-5 materials of Example 1, but using H-ZSM-5 precursor materials with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios of 280, 55, and 30.

### EXAMPLE 5

*Preparation of ZrO<sub>2</sub>/Cu-ZSM-5:* This material was prepared similarly to the CeO<sub>2</sub>/Cu-ZSM-5 material of Example 1, but using a nanoparticle ZrO<sub>2</sub> sol in place of the CeO<sub>2</sub> sol.

### EXAMPLE 6

*Preparation of MoO<sub>3</sub>/Cu-ZSM-5:* This material was prepared similarly to the CeO<sub>2</sub>/Cu-ZSM-5 material of Example 1, but standard incipient wetness of ammonium heptamolybdate salt was used instead of the slurry method.

### EXAMPLE 7

*Preparation of (CeO<sub>2</sub>,ZrO<sub>2</sub>)/Cu-ZSM-5:* This material was prepared similarly to the CeO<sub>2</sub>/Cu-ZSM-5 material of Example 1, but using a 50:50 (by weight) mixture of the CeO<sub>2</sub> and ZrO<sub>2</sub> sols.

**EXAMPLE 8**

*Preparation of Co-ZSM-5:* This material was prepared similarly to the Cu-ZSM-5 sample of Example 1, but using  $\text{Co}(\text{NO}_3)_2$  salt as the cobalt precursor. Additionally, the slurry was gently warmed during the exchange process to ca. 50°C.

**EXAMPLE 9**

*Preparation of  $\text{CeO}_2$ /Co-ZSM-5:* This material was prepared similarly to the  $\text{CeO}_2$ /Cu-ZSM-5 sample of Example 8, but starting with the Co-ZMS-5 sample from Example 7.

**EXAMPLE 10**

*Preparation of  $\text{CeO}_2$ /(Cu,Co)-ZSM-5:* This material was prepared similarly to the  $\text{CeO}_2$ /Cu-ZSM-5 material of Example 1, but instead of only  $\text{Cu}(\text{NO}_3)_2$  solution for the exchange process, a solution containing 0.005M  $\text{Cu}(\text{NO}_3)_2$  and 0.005M  $\text{Co}(\text{NO}_3)_2$  was used for co-exchange.

**EXAMPLE 11**

*Preparation of Cu-MOR and  $\text{CeO}_2$ /Cu-MOR:* These materials were prepared similarly to the Cu-ZSM-5 and  $\text{CeO}_2$ /Cu-ZSM-5 materials from Example 1, but instead of H-ZSM-5 as the precursor material, H-MOR ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 20) was used as the precursor.

**EXAMPLE 12**

*Preparation of Cu-ZSM-5.* Cu-ZSM-5 material was prepared from the ammonium form of ZSM-5 via the exchange of  $\text{Cu}(\text{NO}_3)_2$ . A 0.01M solution of  $\text{Cu}(\text{NO}_3)_2$  was prepared from . Approximately 20g of  $\text{NH}_4$ -ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$ ) was massed into a beaker, and the  $\text{Cu}(\text{NO}_3)_2$  solution was added at a ratio of 10ml/g (ca. 200ml). The slurry was then stirred vigorously while monitoring its pH, typically in the range of pH 2-4. A 0.1M solution of  $\text{NH}_4\text{OH}$  was slowly added drop-wise to the slurry until the pH remained stable near 8.0. The solution was left to stir overnight (>18hrs). After stirring, the solution was filtered then rinsed with distilled water. The collected solids were then dried in an oven at ca. 110°C to remove the bulk of the moisture, then transferred to a calcination oven at 500°C for 3 hours. The sample was then removed and collected. The above process (starting with  $\text{Cu}(\text{NO}_3)_2$  solution addition) was

repeated twice more to increase the exchange level on the Cu-ZSM-5 to about 100%.

### EXAMPLE 13

*Preparation of CeO<sub>2</sub>/Cu-ZSM-5 (Forward, ca. 20wt% loading).* The Cu-ZSM-5 material from Example 12 was used as a precursor to the preparation of the two-phase catalyst. A CeO<sub>2</sub> sol from Nyacol (20% wt) was used as the CeO<sub>2</sub> precursor. Approximately 2g of Cu-ZSM-5 was put into a pyrex dish. CeO<sub>2</sub> sol was added drop-wise into the solid, with vigorous stirring after each drop, until the solid-liquid mixture became paste-like, and the solid material was completely wetted, typically obtained after about 2ml of sol addition. The mixture was placed into an oven at ca. 110°C to remove the bulk of the moisture, and then the remaining solid was collected and transferred to a calcination oven at 500°C for 3 hours. The sample was then removed and collected. This method was called the "forward" method with respect to the order of the copper and ceria loading.

### EXAMPLE 14

*Preparation of CeO<sub>2</sub>/Cu-ZSM-5 (Forward, ca. 40% loading).* A sample was prepared following the methods of Example 13. This precursor material was then subjected to the same medication as outlined in Example 13 as to double the loading of the ceria.

### EXAMPLE 15

*Preparation of CeO<sub>2</sub>/Cu-ZSM-5 (Forward, ca. 10% loading).* This material was prepared similarly to Example 13, but prior to addition, the CeO<sub>2</sub> sol was diluted in half by the addition of an equal amount of water as to reduce the sol concentration to ca. 10w%. This diluted sol was then added in the same fashion as outlined in Example 13.

**EXAMPLE 16**

*Preparation of CeO<sub>2</sub>/ZSM-5 (20% loading).* This material was prepared similarly to Example 13, but using the NH<sub>4</sub>-ZSM-5 form of the zeolite provided as the reagent as opposed to the Cu-ZSM-5 material.

**EXAMPLE 17**

*Preparation of CeO<sub>2</sub>/Cu-ZSM-5 (Reverse, 20% loading).* This material was prepared similarly to Example 12, but using the CeO<sub>2</sub>/H-ZSM-5 material of Example 16 as the initial precursor. Three Cu exchange steps were performed as per Example 12. This method was called the 'reverse' method with respect to the order of the copper and ceria loading.

**EXAMPLE 18**

*Preparation of CeO<sub>2</sub>/Cu-ZSM-5 (Reverse, 40% loading).* Material was prepared as per Example 16. The resulting material was then impregnated again with CeO<sub>2</sub> sol following the sample procedure of Example 16 to increase the ceria loading. Copper was then exchanged onto this material as per Example 17.

**EXAMPLE 19**

*Preparation of CeO<sub>2</sub>/Cu-ZSM-5 (Reverse, 10% loading).* Initial material was prepared similarly to Example 16, but using the diluted sol as per Example 15. Copper was then exchanged onto this material as per Example 17.

**EXAMPLE 20**

*Preparation of Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2</sub> sol.* A 0.08M solution of Ce(NO<sub>3</sub>)<sub>3</sub> and a 0.08M solution of Sm(NO<sub>3</sub>)<sub>3</sub> were mixed in the appropriate ratio to achieve the desired metal oxide composition; for the ratio of Ce:Sm of 4 in the present example, 65ml of the Ce(NO<sub>3</sub>)<sub>3</sub> solution were combined with 16mL of the Sm(NO<sub>3</sub>)<sub>3</sub> solution. The metal hydroxides were coprecipitated as a gel by the drop-wise addition of concentrated ammonium hydroxide until a pH above 9 was maintained. The gel material was filtered and then washed twice with ca. 100mL distilled water followed by one washing with ca. 50mL ethanol. The collected solid was then placed into an oven at

110°C under reduced pressure for 4 hours, which caused the gel to collapse into a glass-like form. The pulverized product was peptized in acetic acid and diluted in distilled water to the desired concentration (20wt% in the present example).

#### EXAMPLE 21

*Preparation of  $Ce_{0.8}Sm_{0.2}O_2$ -Cu-ZSM-5 (Forward, 20% loading).* This material was prepared similarly to Example 13, but using the sol from Example 20 as the sol precursor material.

#### EXAMPLE 22

*Preparation of  $Ce_{0.8}Zr_{0.2}O_2$  sol.* This material was prepared similarly to Example 20, except a 0.08M solution of  $ZrO(NO_3)_2$  was used instead the  $Sm(NO_3)_3$  solution. Additionally, after the vacuum drying, the sample was peptized by dilute nitric acid in a digestion bomb overnight at 135°C; the concentration of the nitric acid was determined based on a ratio of  $NO_3$  to total metal content (Ce and Zr) of 0.25. The suspension obtained was air-dried first and then placed in an oven at 110°C for 30 minutes. The powder was re-dispersed in distilled water and passed through a 0.2  $\mu$  filter. The concentration of the sol was adjusted to 20 wt % oxide.

#### EXAMPLE 23

*Preparation of  $Ce_{0.8}Zr_{0.2}O_2$ -Cu-ZSM-5 (Forward, 20% loading).* This material was prepared similar to Example 13, but using the sol from Example 22 as the sol precursor material.

#### EXAMPLE 24

*DeNO<sub>x</sub> Activity of Samples.* The samples prepared in Examples 1-11 were tested for deNO<sub>x</sub> activity and the results are illustrated on Figures 1-7. The samples prepared in Examples (12-23) were tested for deNO<sub>x</sub> as described below hereafter and the conversion of NO to N<sub>2</sub> over the temperature range of 250-400°C is listed in Table 1.

TABLE 1

Material	Example	NO to N <sub>2</sub> Conversion (%)			
		250°C	300°C	350°C	400°C
Cu-ZSM-5	12	6	18	47	60
CeO <sub>2</sub> /Cu-ZSM-5 (Forward, 20%)	13	40	35	26	20
CeO <sub>2</sub> /Cu-ZSM-5 (Forward, 40%)	14	45	34	22	14
CeO <sub>2</sub> /Cu-ZSM-5 (Forward, 10%)	15	22	50	37	25
CeO <sub>2</sub> /Cu-ZSM-5 (Reverse, 20%)	17	22	64	52	43
CeO <sub>2</sub> /Cu-ZSM-5 (Reverse, 40%)	18	22	55	37	26
CeO <sub>2</sub> /Cu-ZSM-5 (Reverse, 10%)	19	17	59	45	35
Ce <sub>0.8</sub> Sm <sub>0.2</sub> O <sub>2</sub> /Cu-ZSM-5 (Forward, 20%)	21	13	46	38	N/A
Ce <sub>0.8</sub> Zr <sub>0.2</sub> O <sub>2</sub> /Cu-ZSM-5 (Forward, 20%)	23	20	48	30	24

The NO<sub>x</sub> conversion activity was performed as follows. Approximately 150 mg of sample was loaded into a quartz tube, and connected to a gas manifold system. Prior to reaction, the sample was pretreated in He at 500°C for one hour. Gases were available as 5.025% NO in He, 3.0% C<sub>3</sub>H<sub>6</sub> in He, 4.96% O<sub>2</sub> in He, and pure He. The gases were controlled with Brooks 5850e mass flow controllers as to introduce a gas flow of 1000 ppm NO, 1000 ppm C<sub>3</sub>H<sub>6</sub>, 2% O<sub>2</sub>, and the balance He at a space velocity of approximately 30,000 hr<sup>-1</sup>. For water tests, water was pumped into the system with a syringe pump and the water and gas flows were adjusted to give the same concentration of gases above and 10% H<sub>2</sub>O. The reaction was allowed to

proceed at 500°C for 3 hrs prior to taking any readings. The reaction temperature was varied between 200°C and 600°C in 50°C increments, allowing for at least 30 minutes at temperature before analyzing the effluent. The reaction effluent was analyzed using an MTI micro gas chromatograph with molecular sieve 5 Å and poropak Q columns for the stationary and hydrocarbon gases, or with a California Analytical Instruments NO<sub>x</sub> detector, model HCLD-400, for the NO and NO<sub>2</sub>.

The reduction of NO<sub>x</sub> and C<sub>3</sub>H<sub>6</sub> over Cu-ZSM-5 and ceria on ZSM-5 are shown on Figure 1. As can be seen, at about 350°C, the zeolite supported copper shows a NO<sub>x</sub> conversion under wet conditions of just under 20% whereas the ceria and zeolite shows an NO<sub>x</sub> conversion under wet conditions of just under 10%.

Referring to Fig. 2, it can be seen that the combination of a zeolite supported copper and ceria catalyst provides NO<sub>x</sub> conversions in the presence of water in excess of 40% at about 350°C for both the silicon to aluminum ratios displayed in Fig. 2, that is a silicon to aluminum ratio of 67 and a silicon to aluminum ratio of 45. These conversions are outstanding. Only small amounts of NO<sub>2</sub> (< 10ppm) were observed, and no other nitrogen oxide species was present. Carbon dioxide was the only observable product from C<sub>3</sub>H<sub>6</sub> oxidation. The Cu-ZSM-5/CeO<sub>2</sub> catalyst had slightly lower maximum NO<sub>x</sub> activity than the Cu-ZSM-5. In all cases, the maximum NO<sub>x</sub> conversion approaches the temperature when the propene is nearly all consumed.

Under wet conditions, the Cu-ZSM-5 catalyst shows significant loss in NO<sub>x</sub> and hydrocarbon conversion activity. The CeO<sub>2</sub>/Cu-ZSM-5 catalyst shows improved NO<sub>x</sub> activity under wet conditions, possessing NO<sub>x</sub> conversion levels over 40%.

After reaction, the used catalysts were examined in the reactor prior to removal. It was noted that Cu-ZSM-5 catalyst showed significant discoloration throughout the bed, indicative of coking. However, with the other catalysts tested, it was observed that only a small fraction of the bed length was discolored, the rest of the bed remaining the same color as the original sample.

The ceria improves the Cu-ZSM-5 in two ways. First, it provides necessary water stability. Ceria also aids the  $\text{NO}_x$  conversion reaction, based on improved activities with the  $\text{CeO}_2/\text{Cu-ZSM-5}$ .

Fig. 3 shows similar data for a catalyst comprised of a zeolite supported copper with zirconia and a zeolite supported copper with molybdenum oxide. In these data it is clear that the zirconia containing catalyst is a superior performer at lower temperatures such as  $400^\circ\text{C}$ , whereas at  $450^\circ\text{C}$ , the molybdenum containing catalyst is very good.

Fig. 4 shows a comparison of a cobalt and a combination of a zeolite supported cobalt with ceria. As can be seen from the data, without the ceria present there is little, if any,  $\text{NO}_x$  conversion under wet conditions whereas with the ceria present there is substantial conversion at  $450^\circ\text{C}$ .

Fig. 5 shows data for a variety of catalyst, the first being a zeolite supported copper with a combination of ceria and zirconia which shows excellent  $\text{NO}_x$  conversions under wet conditions at about  $400^\circ\text{C}$  and acceptable but less conversions at  $350^\circ\text{C}$ . Similarly, the copper cobalt supported zirconia with ceria shows excellent  $\text{NO}_x$  conversions under wet conditions both at  $400^\circ$  and  $350^\circ\text{C}$ .



Fig. 6 illustrates comparisons of a mordenite supported copper and a mordenite supported copper with ceria under both wet and dry conditions. It is seen that the inventive catalyst, that is the copper supported mordenite with ceria has clearly superior activity at temperatures under 400° compared to the copper supported mordenite.

Finally in Fig. 7, shows data for a physical mixture of ceria and Cu-ZSM-5 and Cu-ZSM-5 on ceria. Note that these catalysts were tested at a space velocity of 10,000 Hr<sup>-1</sup> and 20% water when present. The physical mixture of Cu-ZSM-5 and CeO<sub>2</sub> showed no loss in activity, but only a slight shift in temperature where the maximum activity occurred. In the case of Cu-ZSM-5/CeO<sub>2</sub>, there is still some loss of NO conversion, but not as great as the Cu-ZSM-5 alone, while hydrocarbon conversion remained high.

Figures 8 and 9 are Scanning Electron Microscopy (SEM) of a zeolite without the stabilizing oxide (see Fig. 8) and a zeolite with a coating of the stabilizing oxide (Fig. 9). As seen from the two SEMs, the stabilizing oxide entirely coats the zeolite applied by the method hereinbefore set forth adding the oxide in the form of colloidal sol.

The possible concentration ranges for the metal salt solution in the range of from 0.001M to about 1M solutions, but preferably in the range of 0.01M to 0.1M. The pH of the zeolite/solution slurry will typically start in the pH range from 2 to 5; the pH of the solution can be raised as high as 12 with ammonia hydroxide solution, but is typically only raised to a pH between 6 and 8. Certain metal salts, such as Co(NO<sub>3</sub>)<sub>2</sub>, will exchange better at higher temperatures; when used, the slurry is taken to

temperatures between 50 and 80°C in a refluxing unit during the exchange process. All of these variables can be used to influence the rate, quantity, and quality of the metal exchange process on the zeolite.

Nanoparticle sols can be obtained through many industrial sources; however, it is sometimes necessary to prepare these sols directly as illustrated in Example 2 and others, particularly in the case of mixed metal oxides. By nanoparticles, we mean particles having an average diameter of less than about 100 nanometers and preferably in the range of from about 20 to about 40 nanometers. In any event, the oxides prepared from these sols should have diameters larger than the pore sizes of the molecular sieves, so that the stabilizing oxides do not enter the sieve but coat same. Generally, these sols are made by the peptization of a dry oxide gel in an acidic medium. The oxide gel can be prepared by a number of procedures, most commonly by (co) precipitation of the metal hydroxide from a solution of the metal salts by ammonium hydroxide. For mixed metal sols, the desired metal ratio in the final sol can be controlled by the appropriate mixing of the initial metal salts. Additional information on sol formation can be found in D.-H. Tsai and T.J. Huang, *Appl. Catal. A.*, **223**, 1-9 (2002), and J.L. Woodhead, U.K. Patent 2102780.

The data reported herein were for lean-burn combustion gases, that is combustion gases in which air or oxygen was present in greater than stoichiometric quantities. Moreover, all the data reported herein had between about 10 and 20% by volume water present in the combustion gases. However, the inventive catalyst is operable in either rich or lean burn conditions with or without water. Currently, the best conditions for NO<sub>x</sub> remediation is with C:N ratios of from 1:1 to 16:1. Gas mole

to gas mole ratios of 1:1 to 10:1 are preferred. Space velocities from 1,000 hr.<sup>-1</sup> to about 100,000 hr.<sup>-1</sup> are estimated with space velocities of 30,000 hr.<sup>-1</sup> having been measured. Moreover, essentially all the remediated NO<sub>x</sub> is converted to N<sub>2</sub> with little if any N<sub>2</sub>O being produced.

Accordingly, two phase catalysts prepared according to the methods of Examples 1 to 11 herein are molecular sieves having pore sizes up to about 8 Å supporting one or more transition metals, with the molecular sieve particles coated by a stabilizing oxide. Examples 12 to 23 herein illustrate additional formations of the inventive two phase catalysts and method of making same. Not only are the catalysts distinctive for their two phase formation, but the oxide coating herein disclosed provides the unusual catalytic activity with layer oxide loadings than heretofore available. Oxide loadings of 40% by weight are reported in Table 1 and it is believed loadings of about 50% by weight can be obtained. Valuable catalytic materials with oxide loadings of up to 10% by weight but preferably, up to about 20% by weight have been used.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A two phase catalyst comprising one or more transition metals supported on a molecular sieve and one or more stabilizing oxides coating the molecular sieve.
2. The catalyst of claim 1, wherein the molecular sieve has a pore size not greater than 8 Å.
3. The catalyst of claim 1, wherein the molecular sieve is a zeolite.
4. The catalyst of claim 3, wherein the zeolite has a pore size between 4 and 8 Å.
5. The catalyst of claim 3, wherein the zeolite is an aluminosilicate.
6. The catalyst of claim 5, wherein the zeolite includes one or more of zeolite Y, zeolite beta, ZSM-5, ZSM-12, mordenite, or ferrerite.
7. The catalyst of claim 5, wherein the zeolite has a silicon-to-aluminum ratio between about 17 and about 238.
8. The catalyst of claim 1, wherein the transition metal includes one or more of Cu, Co, Fe, Ag, and Mo.
9. The catalyst of claim 8, wherein the transition metal is Cu.
10. The catalyst of claim 8, wherein the transition metals are present in the catalyst up 200% by weight.

11. The catalyst of claim 10, wherein the stabilizing oxides includes one or more of the oxides of Zr, Mo, V, Nb, or the rare earths.
12. The catalyst of claim 11, wherein the stabilizing oxide is  $\text{CeO}_2$ .
13. The catalyst of claim 12, wherein the stabilizing oxides are present in the catalyst not less than about 20% by weight.
14. The catalyst of claim 1, wherein the transition metal supported molecular sieve and the stabilizing oxide are physically mixed when the stabilizing oxide is in the form of a sol.
15. The catalyst of claim 14, wherein the stabilizing oxide coats the outside of the molecular sieve.
16. The catalyst of claim 1, wherein the molecular sieve is contacted by a stabilizing oxide sol with particles between about 20 to about 40 nanometers in diameter.
17. A two phase catalyst comprising one or more transition metals of Cu, Co, Fe, Ag and Mo supported on a molecular sieve having a pore size not greater than 8 Å and a stabilizing oxide of one or more of the oxides of Zr, Mo, V, Nb or the rare earths coating the molecular sieve.
18. The catalyst of claim 17, wherein the transition metal is Cu.
19. The catalyst of claim 17, wherein the stabilizing oxide is  $\text{CeO}_2$ .
20. The catalyst of claim 17, wherein the transition metal is Cu and the stabilizing oxide is  $\text{CeO}_2$  and the molecular sieve is ZSM-5.

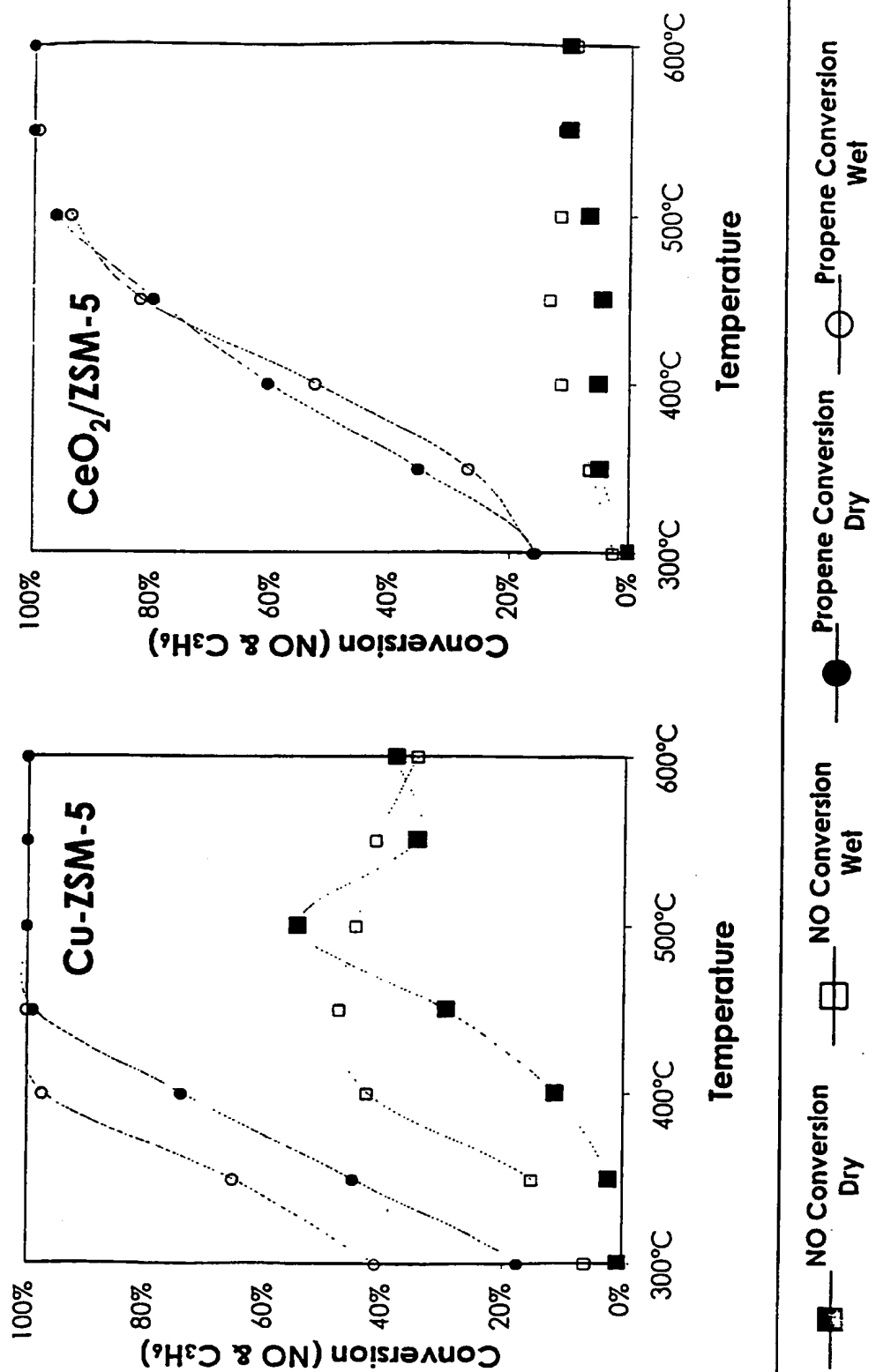
21. The catalyst of claim 20, wherein the Cu is present up to about 10% by weight of the catalyst and the CeO<sub>2</sub> is present up to about 40% by weight of the catalyst.

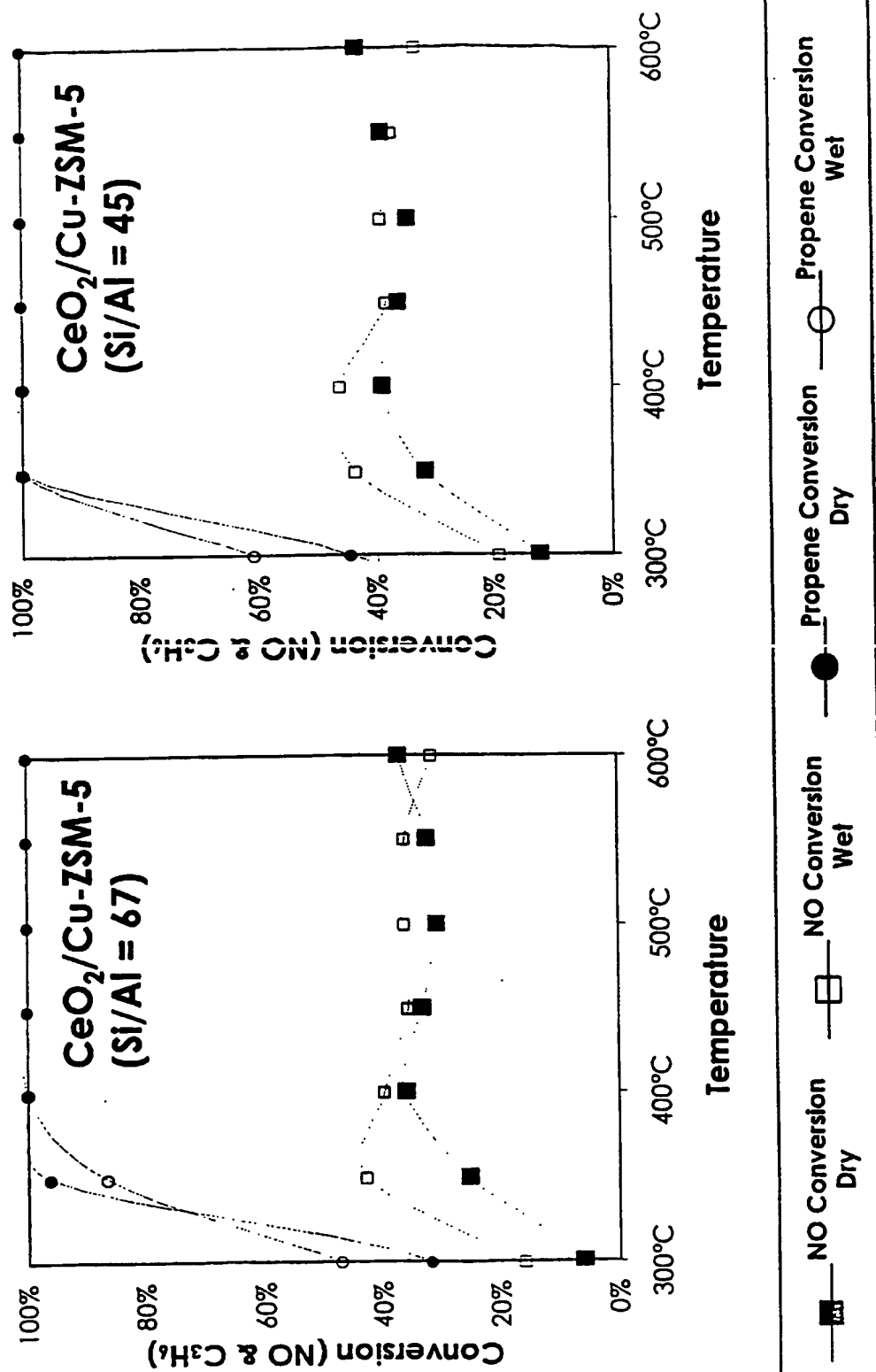
22. A method of remediating the concentration of nitrogen oxides (NO<sub>x</sub>) in a combustion exhaust stream by contacting the exhaust stream with one or more reductants at a temperature not greater than 600°C over a two-phase catalyst comprising one or more transition metals supported on a molecular sieve and one or more stabilizing oxides coating the molecular sieves.

23. A method of remediating the concentration of nitrogen oxides (NO<sub>x</sub>) in a combustion exhaust stream by contacting the exhaust stream with one or more organic reductants in the presence of water at a temperature not greater than 600°C over a two phase catalyst comprising one or more transition metals of Cu, Co, Fe, Ag and Mo supported on a molecular sieve having a pore size not greater than about 8 Å and a stabilizing oxide of one or more of the oxides of Zr, Mo, V, Nb or the rare earths coating the molecular sieve and present in an amount of up to about 40% by weight.

24. A method of preparing a two phase catalyst comprising contacting a molecular sieve material having a pore size less than about 8 Å with a sol of oxide particles having average diameters of greater than 8 Å and less than about 100 nanometers to coat the molecular sieve particles with the oxide particles and loading the molecular sieve before and/or after the oxide coating with one or more transition metals.

25. A two phase catalyst made according to the method of claim 24.

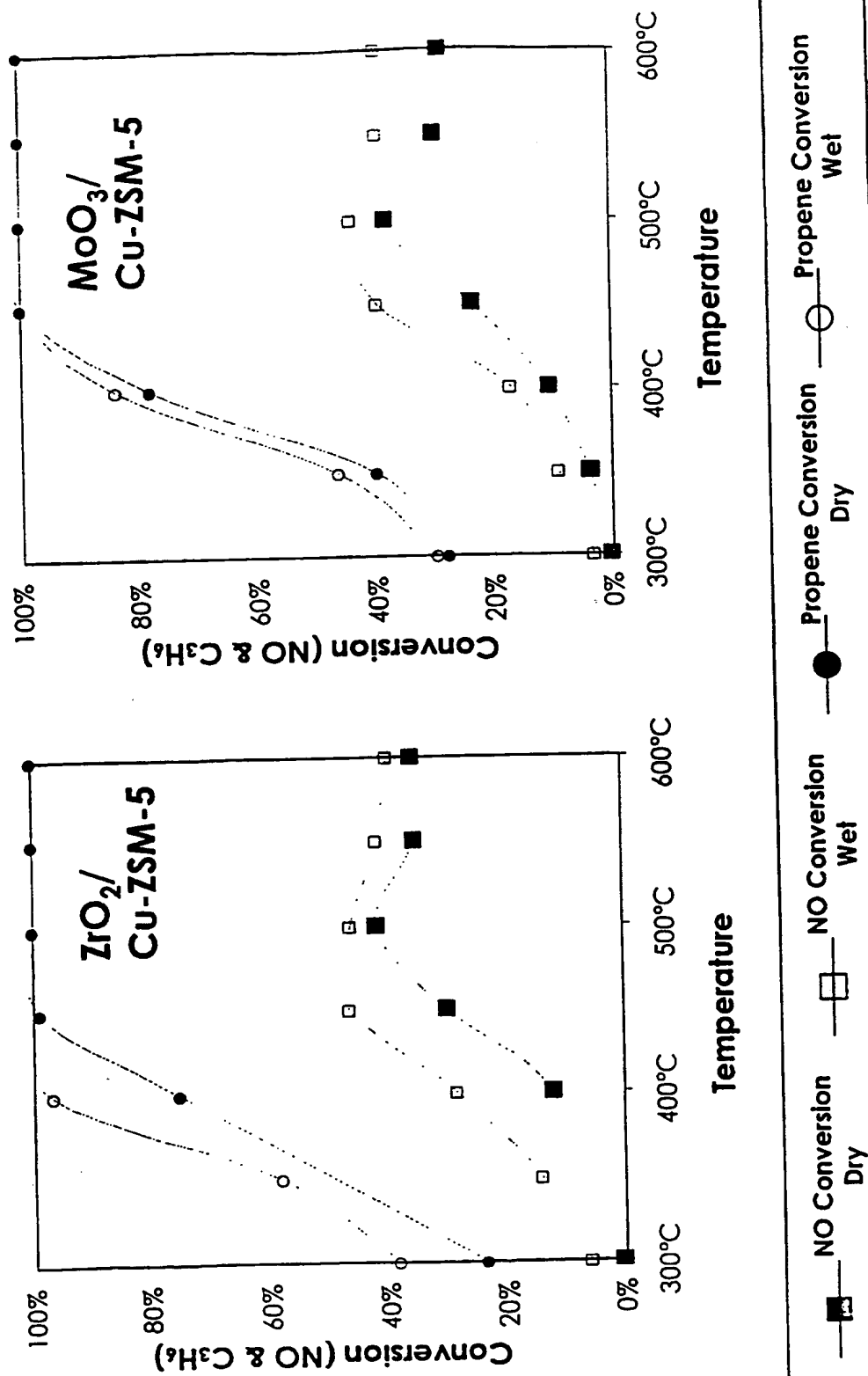
**Figure 1**

**Figure 2**

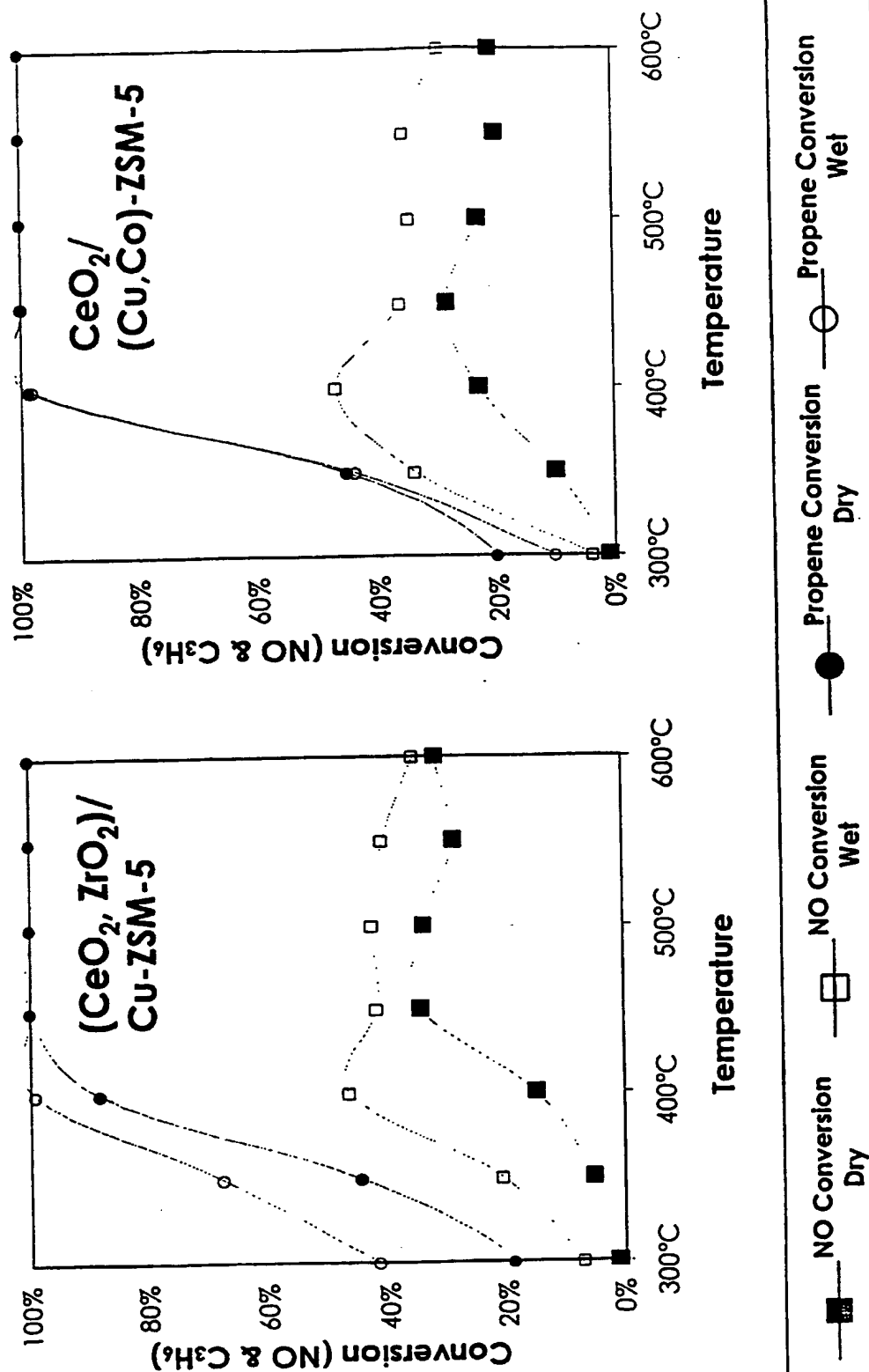


3/9

Figure 3





**Figure 5**

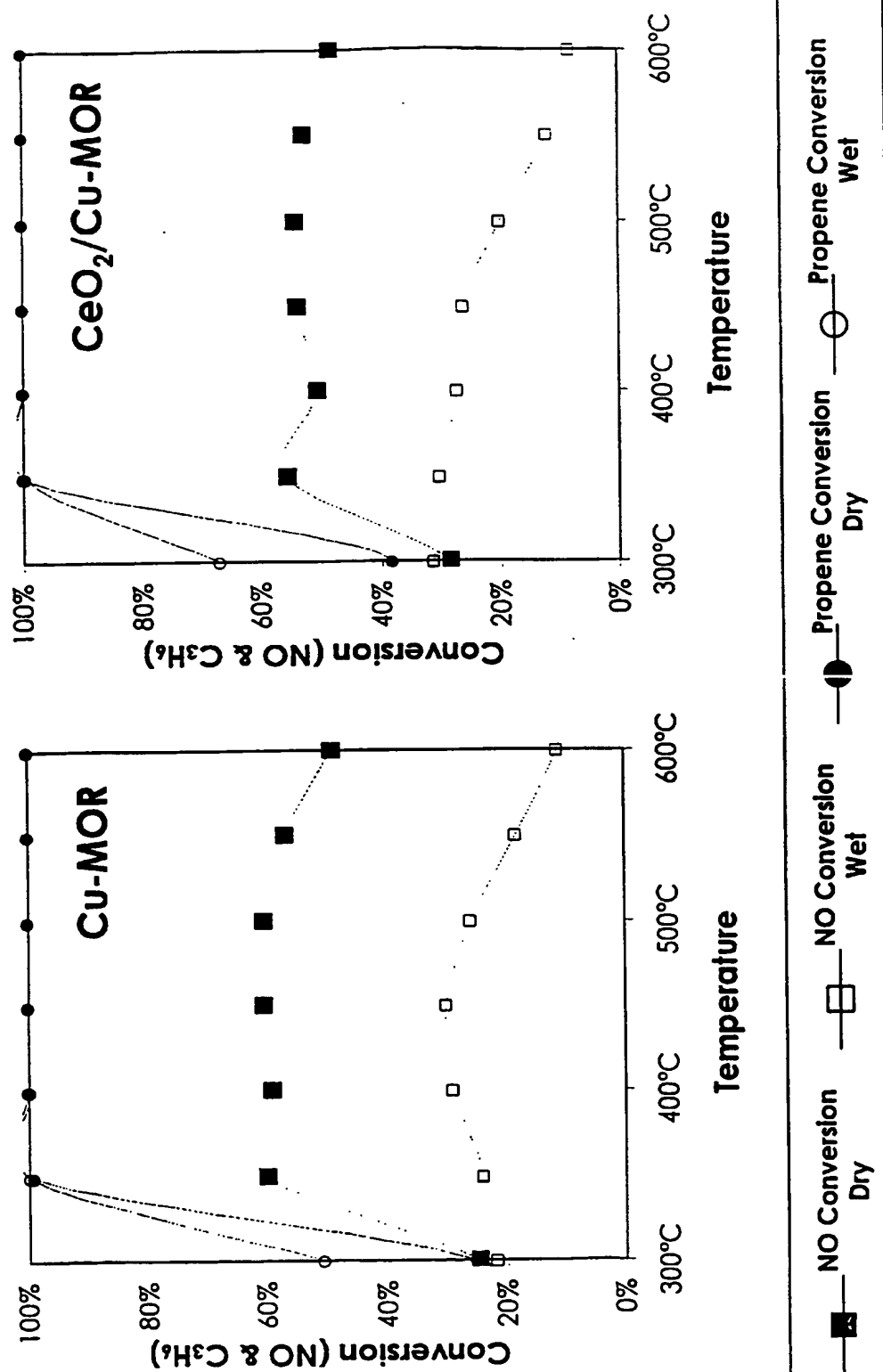
**Figure 6**

Figure 7

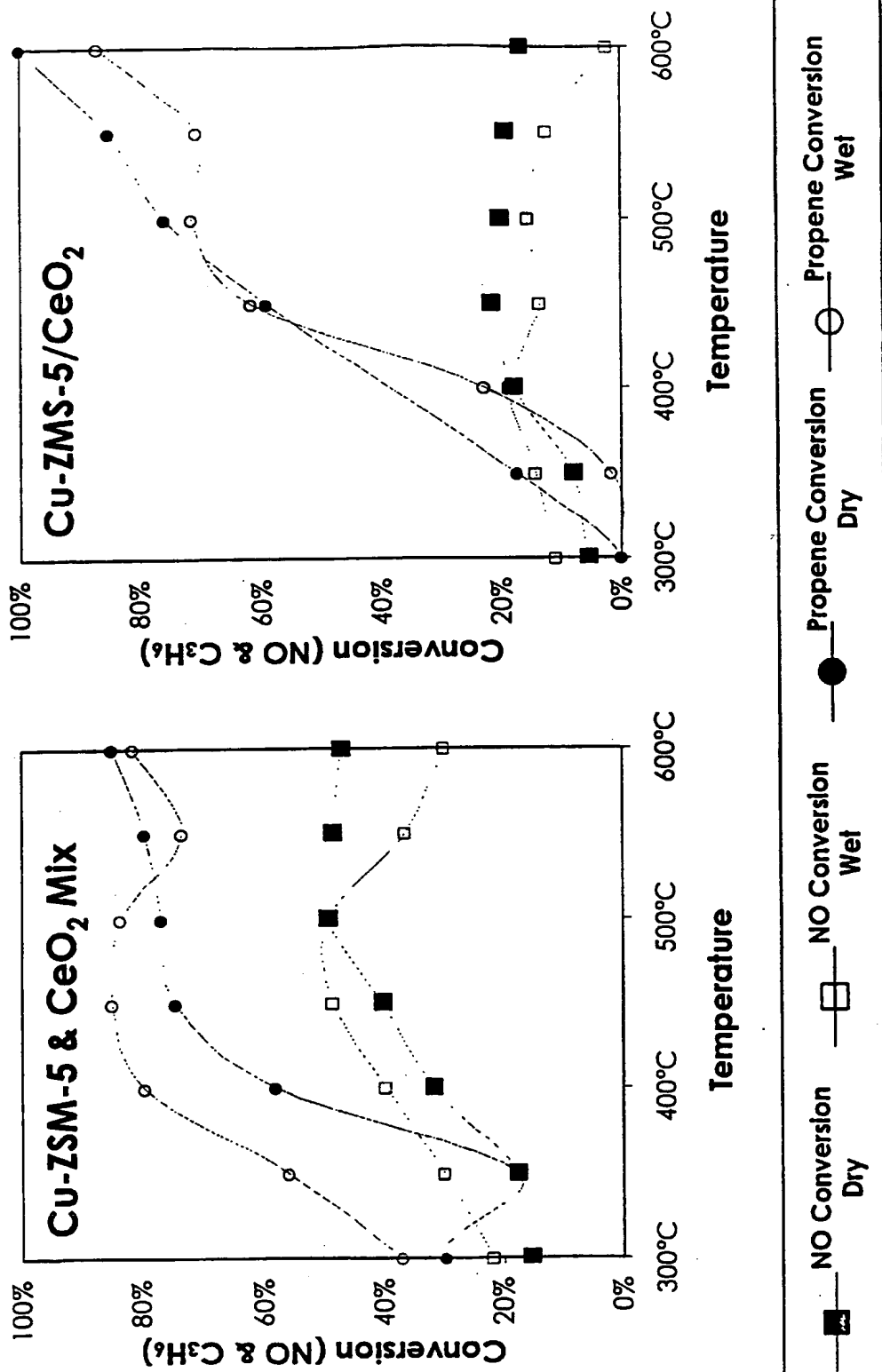




FIGURE 8



FIGURE 9

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/07047

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01J 29/08, 29/14, 29/16, 29/40, 29/46, 29/48, 29/65, 29/68, 29/69, 29/70, 29/76, 29/78  
US CL : 502/64, 65, 66, 73, 74, 77, 78, 79; 423/239.2

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/64, 65, 66, 73, 74, 77, 78, 79; 423/239.2

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,116,586 A (BAACKE et al) 26 May 1992 (26.05.1992), columns 3-10.	1-25
X	US 4,962,075 A (GREEN et al) 09 October 1990 (09.10.1990), columns 3-8.	1-25
X	US 5,276,249 A (GREENE et al) 04 January 1994 (04.01.1994), columns 2-18.	1-21, 24-25
---		-----
A		22-23
X	US 6,143,681 A (SACHTLER et al) 07 November 2000 (07.11.2000), columns 2-6.	1-25

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

27 June 2003 (27.06.2003)

Date of mailing of the international search report

23 JUL 2003

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, Virginia 22313-1450

Facsimile No. (703)305-3230

Authorized officer

Christina Ildebrando

Telephone No. (703) 308-0654



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☒ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**